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Test Method

Dispersed particle size characterization by in-line turbidimetry during polymer extrusion

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ABSTRACT

The presence of a dispersed second phase in a medium scatters light, attenuating the transmitted light intensity. This effect is maximized when the average particle size matches the light's wavelength. This work proposes an in-line optical detector which measures the attenuation of the transmitted light intensity by illuminating the medium with different monochromatic light wavelengths. Curves of normalized turbidity as a function of the dispersed particle size were simplified to a Gaussian behavior. We propose a Z parameter, function of the ratio between the transmitted light intensity measured under a particular illuminating color compared to that measured under infrared illumination, which is proportional to the particle size. The method was bench validated employing alumina particles aqueous suspensions with known particle size and during polystyrene melt extrusion traced by alumina particles and polyolefin dispersed second phase. The estimated particle sizes measured in-line during the extrusion, were in good agreement with the reference alumina particles.

1. Introduction

The extrusion process is widely employed for the preparation of polymer mixtures and composites, when all components are dispersed in the molten polymeric matrix. It is desirable that the second phase be evenly dispersed and distributed. Reduction in the particle size of the dispersed second phase generally acts in favor of the material's mechanical properties, therefore, coarse particle agglomerates should be avoided [1].

Great effort has been made to develop *in situ* and/or *in real time* characterization techniques in which the morphology could be monitored along the main flow stream of the extruder during processing [2–7]. Among the available techniques, there are those based on reo-optic characterization of the polymer flow in which its optical extinction, namely the attenuation of a light beam intensity while passing through the polymer medium, is analyzed.

When light penetrates the matter, four phenomena may result from their interaction [8,9]: a) part of the radiation may be reflected at the interface between the two media (I_R), b) part of the radiation may be refracted, i.e., transmitted through the material with change in the propagation direction (I_T), c) part of the radiation may be transmitted without change of the propagation direction (I), and d) part of the radiation may be absorbed (I_A). The reflected and refracted components are taken as light scattering, which is characterized by changes in the radiation's propagation direction. Then, the attenuation of the light beam with incident light intensity I_0, while interacting with the matter, is given by Eq. (1).

$$I_0 - I = I_R + I_T + I_A \tag{1}$$

I_R and I_A being the reflected and the absorbed light beam intensity and, I_T and I, the transmitted light beam intensity with and without change in the propagation direction, respectively.

Particles of the micrometric range attenuate the incident light by light scattering with low reflection, whereas molecules of nanometric size are impenetrable to the light transmission, mainly due to light attenuation through absorption [10–12]. The portion of radiation that is transmitted is the subject of turbidimetry.

There are many theories describing a light beam's attenuation by light scattering, among them, spherical scatters (droplets and particles), highlighting the Rayleigh's and Mie's theories, are the most suitable. The Mie scattering theory converges to the limit of geometric optics for large particles and has no size limitations. Hence, most spherical particle scattering systems, including Rayleigh's scattering, are described through Mie's theory [8]. This theory states that the transmitted light

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extinction is maximized when the average size of the suspended particles is in the same range as the incident light's wavelength. The contribution from either smaller or bigger particles is consistently attenuated until no measurable effect is seen [13]. Although the solution proposed by Mie is caused by a single spherical particle, it may also be applied to particles that are randomly dispersed and further apart than a light's wavelength [14].

Mie's theory of light scattering by spherical particles postulates that the turbidity is a function of the dispersed phase concentration, particle size, light wavelength and refractive index ratio of both phases. For spherical particles of radius R, the turbidity is given by Eq. (2) [15].

$$\tau = N\pi R^2 Q_S \tag{2}$$

Q_s being the scattering coefficient, N the number of monodisperse particles per volume as Eq. (3).

$$N = \frac{\varphi_d}{\left({}^4\!/_3\right)\pi R^3} \tag{3}$$

in which φ_d is the volumetric fraction of the dispersed phase.

The scattering coefficient is a function of the refractive index ratio of the particle n_1 to the medium n_2 and the ratio of particle circumference to wavelength of light ($\pi D/\lambda$). Bohren and Huffman [8] and Van de Hulst [16] have presented a procedure to obtain it, summarized in Eq. (4).

$$Q_S = \frac{2}{x^2}(|a_j|^2 + |b_j|^2)\sum_{j=1}^{\infty}(2j+1) \tag{4}$$

Being $x = 2\pi R/\lambda$, is the diffraction parameter and a_j, b_j are Mie's coefficients expressed in terms of the Riccatty-Bessel functions $\Psi_j(t)$ and $\xi_i(t)$ which are expressed in terms of the Bessel functions of non-integer order. However, owing to the complexity of the Mie scattering formulation and its solution, Rayleigh scattering theory is normally preferred and used when applicable [17].

Under elastic Rayleigh scattering, the scattered intensity of electromagnetic radiation is a function of the observer distance, a, from the center of the particle of radius R, and the scattering angle θ, which is measured relative to the propagation direction of the incident radiation. The scattered intensity I from a spherical particle is defined by Eq. (5) [17].

$$I = I_0\left(\frac{1+\cos\theta}{2a^2}\right)\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2 R^6 \tag{5}$$

I_0 being the incident radiation intensity, n the particle refractive index and λ the radiation's wavelength.

Analyzing Eq. (5), one can realize that the scattering intensity is a function of the particle diameter (as radius R) and an inverse function of the illuminating radiation wavelength used [18]. In this regard, plots of specific turbidity as a function of the particle size of the dispersed (scattering) phase go through a maximum when the particle size is close to the radiation's wavelength (light color) used. In the visible wavelength range (400–700 nm), particles with size in this same range will produce the maximum scattering and are normally used as hiding pigments which confer opacity on a coating.

This paper focuses on in-line particle size evaluation during the extrusion process of a dispersed second phase (polypropylene or polyethylene) in a flow of polystyrene molten matrix by quantifying the attenuation of the transmitted light intensity due to light scattering. The light attenuation of aqueous standard size alumina particles was used as reference.

2. Experimental

2.1. Materials

The polymers used in this work were commercial grades of a high molecular weight general purpose polystyrene provided by Innova (Brazil) code N2560, a high melt flow rate homopolypropylene by Braskem (Brazil) code H301 and a medium molecular weight low density polyethylene by Dow (Brazil) code 955I. The feedstock alumina powder code A1000-S was provided by Alcoa (Brazil).

2.2. Double screw extruder

The polymer dispersion was done in a co-rotational twin-screw extruder ZSK 30 from Werner & Pfleiderer with K-Tron gravimetric feeders and a slit-die fitted at the exit. The processing conditions were kept constant during all extrusions, set at: mass flow rate of 2 kg/h, screw rotation speed of 90 rpm, 2KB45 screw profile containing two kneading elements with 45°, and a constant temperature profile along the whole extruder fixed at 220 °C, apart from the feeding zone which was kept at 190 °C. The measurements, such as residence time distribution RTD curves, were made in the transient state in which the second phase is added to the flowing polymer as a pulse while maintaining unchanged all extrusion processing parameters. The presence of the second phase is recorded in real time while it exits the extruder via an in-line optical detector on a slit-die fitted at the extruder exit. More detailed information concerning this in-line optical setup can be obtained in previous publications [10,11,19].

2.3. Extruder slit-die

A slit die was specially developed, made in a modular form, having two modules (upper and lower), separated by two spacers forming the slit in which the molten polymer flows. This allows its thickness to be adjusted to any value between 0.5 and 4 mm. In this work, the slit parameters were kept constant with thickness at 1.5 mm and width at 15 mm. It has two pairs of transparent windows of borosilicate glass with 10 mm diameter and 1 mm thickness in each side of the slit-die, over which the in-line optical detection system is fitted [19].

2.4. In-line optical detector system

The in-line optical detector is placed over the slit-die windows, orthogonally to the flow's direction. In one side is positioned the light source, constituted of four light emitting diodes LED of different monochromatic wavelengths, blue (440 nm), green (575 nm), red (630 nm) and infrared (940 nm), and, at the other side there is a single phototransistor in order to collect the transmitted light intensity of each color, which are switched on and off individually and sequentially. The light exiting the LED passes through the first transparent window, through the measuring medium (aqueous suspension or molten polymer stream), is attenuated by the light scattering of the suspended particles, exits through the second transparent window and, lastly, reaches the phototransistor. Changes in the transmitted light intensity are collected by software, developed in Labview 8.6 (National Instruments) platform for data collection, real-time calculation, screen presentation and data archiving. This optical configuration with four LED's and one phototransistor is an improvement based on a previous setup [20].

2.5. Experimental procedure

2.5.1. Preparation of the alumina reference particles

Given the need to evaluate the light scattering in systems with well-defined dispersed particle sizes, we chose to analyze dispersions of ceramic particles in a polymeric matrix. Alumina powder Al_2O_3 was chosen as a reference standard because it has a refractive index (1.76) which forms a suitable ratio (1.1) with the refractive index of polystyrene (1.59), used as polymer matrix [21].

Since the original alumina feedstock has a broad particle size distribution (PSD), it was necessary to fractionate it in order to obtain samples with specific average diameter and narrow PSD to serve as